

Ab Initio Study of Cyclic Siloxanes (H₂SiO)_n: n = 3, 4, 5

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ABSTRACT

The geometry optimizations for several conformations of tri-, tetra-, and pentacyclosiloxane (H₂SiO)_n (n = 3, 4, and 5) were carried out, and the relative stabilities were compared at the Hartree–Fock (HF) and second order perturbation theory (MP2) levels of theory using the 6-31G* and 6-311G(d, p) basis sets. At the highest levels of theory, the only minimum for n = 4 (D₄) occurs at the highly symmetric D_{4h} structure. In contrast, several, nearly isoenergetic, minima are found on the D₅ surface. These have C₁, C₂, C_s, and D_{5h} symmetries. While the C₁ structure has the lowest MP2/6-311G(d, p) energy, this species is predicted to be highly fluxional, and the distribution of isomers is dependent on temperature. © 1996 by John Wiley & Sons, Inc.

Introduction

The practical importance of cyclosiloxanes is well known,¹ and the structures and the nature of the Si—O bond have been thoroughly investigated, both experimentally and theoretically.² Systems consisting of pentacyclosiloxane cores are of interest as stationary phases for read–write optical storage media, photochromic and photosensitive media, and for application in optical processing devices.³ Especially for cyclodis-

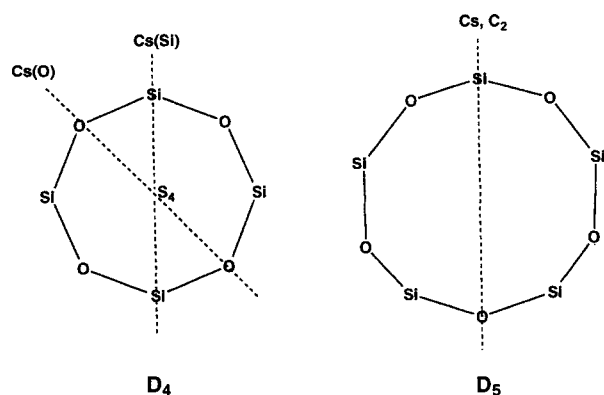
iloxanes (n = 2), considerable interest has been focused on the bonding nature of Si—Si because of the markedly short distance (231 pm) in tetramethylcyclodisiloxane observed by West et al.⁴ For the larger cyclosiloxanes experimental X-ray⁵ and electron diffraction^{6,7} geometries are available. Furthermore, some theoretical predictions of geometries, obtained using molecular mechanics⁸ and *ab initio* electronic structure methods,^{5,8b,9–12} have been performed for limited conformations. However, the use of higher levels of theory has been limited due to the molecular size and the flatness of the potential energy surfaces.

We report here *ab initio* calculations on several conformations of the D_n (H₂SiO)_n species (n = 3, 4, and 5), including electron correlation effects with flexible basis sets. All geometries are fully optimized at the Hartree–Fock (HF) level of theory, with the 6-31G*¹³ and 6-311G(d, p)¹⁴ basis

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SCHEME 1.

sets. The stationary points have been characterized from their harmonic vibrational frequencies (all real for minima; one imaginary for transition states) using the GAMESS¹⁵ and GAUSSIAN92¹⁶ programs. The largest number of basis functions in the present study is 290 (D_5). Calculations on these large species were facilitated by the use of the parallel features of GAMESS.¹⁵ Furthermore, to obtain more reliable energetics, single point calculations were carried out by means of second order Møller–Plesset (MP2) perturbation theory.¹⁷ In addition to obtaining a better understanding of the nature of the potential energy surfaces for these species, a further motivation is to make use of these *ab initio* calculations as an aid to constructing improved molecular mechanics force fields.

Results and Discussion

Cyclosiloxanes can be regarded as oligomers of the siloxane unit ($-\text{SiOH}_2-$) or silanone ($\text{H}_2\text{Si}=\text{O}$), the silicon analog of formaldehyde. Therefore, following previous studies, we will use the notation D_n ($n = 3, 4$, and 5) throughout this article, where D represents a siloxane unit ($-\text{SiOH}_2-$).

As shown in Scheme 1, we have considered several conformations for D_4 and D_5 , but only the D_{3h} conformer has been investigated for D_3 . The optimized geometries are displayed in Figures 1 to 3. Four and five stationary points (minima) were located for D_4 and D_5 , respectively, at the HF/6-31G* level of theory. Using this basis set, the C_1 conformation of D_4 has converged to the $C_5(\text{Si})$ structure, while the other four conformations (D_{4h} , S_4 , $C_5(\text{Si})$ and $C_5(\text{O})$) remain distinct, but very

close in energy. When the basis set is improved to 6-311G(d, p), all of these structures are found to converge to the planar D_{4h} conformation.

The experimental geometry determined by electron diffraction for $(\text{Si}(\text{Me})_2\text{O})_3$ has a Si—O bond length of 1.635 Å and a Si—O—Si angle of 131.6° .⁷ These are in excellent agreement with the HF/6-311G(d, p) predictions. Two electron diffraction structures are available for $D_4(S_4)$: $R(\text{SiO}) = 1.622$ Å and $\text{SiOSi} = 144.8^\circ$ in $(\text{Si}(\text{Me})_2\text{O})_4$,⁷ and 1.628 Å and 148.6° in $(\text{SiH}_2\text{O})_4$.⁶ The HF/6-311G(d, p) bond length of 1.626 Å is bracketed by these two results, while the predicted SiOSi angle is about 12° larger than the experimental ones. To our knowledge, there have been no experimental structure determinations for D_5 .

Note that, for the planar D_{nh} structures, the HF/6-311G(d, p) Si—O distance decreases as ring size increases: 1.642 Å ($n = 3$) > 1.626 Å ($n = 4$) > 1.621 Å ($n = 5$), while the Si—H bond length does not change significantly. On the other hand, the SiOSi bond angle is found to expand significantly as ring size becomes large, while the expansion of the OSiO bond angle is relatively small. These trends have been noted previously for analogous cage compounds.¹⁸

At the HF/6-31G* level of theory, five conformations are found for D_5 , as shown in Tables I and II. When the level of theory is improved to HF/6-311G(d, p), all of these structures retain their distinct identities, except the C_{5v} structure. The latter has converged to the D_{5h} structure. However, the HF/6-311G(d, p)-optimized geometries of the C_5 and C_2 are much closer to that of D_{5h} than are the corresponding HF/6-31G* structures. All of their Si—O (1.621 Å) and Si—H (1.472 Å) distances are the same as those in D_{5h} , and the averaged OSiOSi dihedral angles in C_5 (C_2) decrease from 71.3° (50.9°) to 24.9° (25.7°) when the basis set is improved. On the other hand, the C_1 structure retains a distinctly nonplanar arrangement when the basis set is improved, although it is similar to C_2 . Therefore, we might group the four structures into “ D_{5h} -like” (D_{5h} , C_5) and “ C_2 -like” (C_2 , C_1) conformations for D_5 at this level of theory. The normal vibrational analyses show that the D_{3h} , D_{4h} , and all four conformations of D_5 (D_{5h} , C_5 , C_2 , and C_1) are minima on their respective potential energy surfaces. The lowest vibrational frequencies of D_5 at the HF/6-311G(d, p) level are very small: 7.3 (D_{5h} , degenerate), 7.5 (C_5), 7.0 (C_2), and 11.8 (C_1) cm^{-1} . In each case, as shown in the end-on views in Figure 4, these modes correspond to out-of-plane

motions, relative to the plane defined by the heavy atoms in D_{5h} symmetry. Indeed, the floppiness of the D_5 potential energy surface is emphasized by the existence of nine vibrational modes in each conformer with frequencies less than 100 cm^{-1} .

The calculated energy differences among the conformations of D_4 and D_5 are very small, as expected (see Table II). At the HF/6-31G* level of theory, the S_4 and C_1 structures are the most stable among the conformations of D_4 and D_5 ,

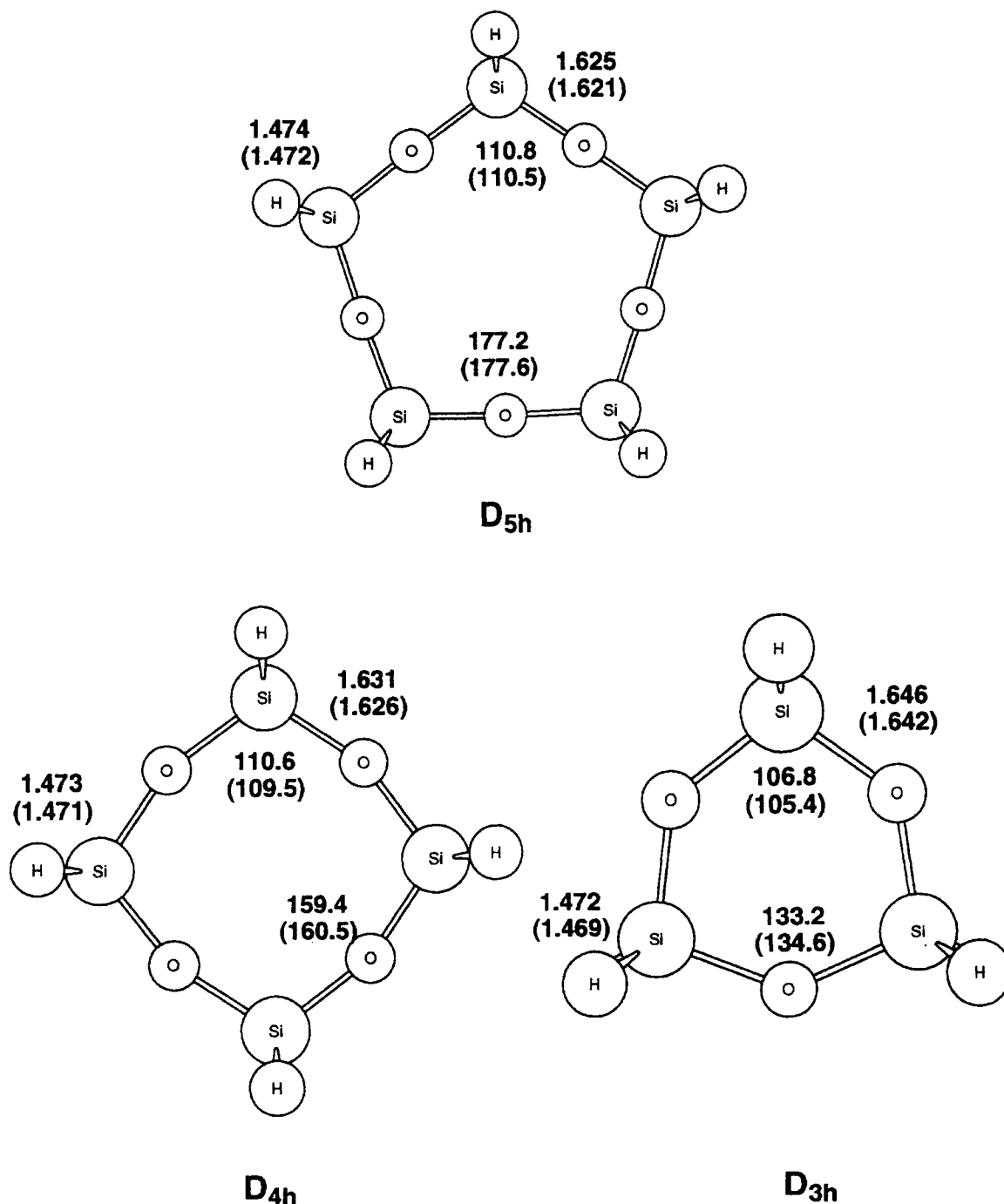


FIGURE 1. The HF/6-311G(*d, p*)-(in parentheses) and HF/6-31G*-optimized geometries of D_{nh} ($n = 3, 4$, and 5) in angstroms and degrees.

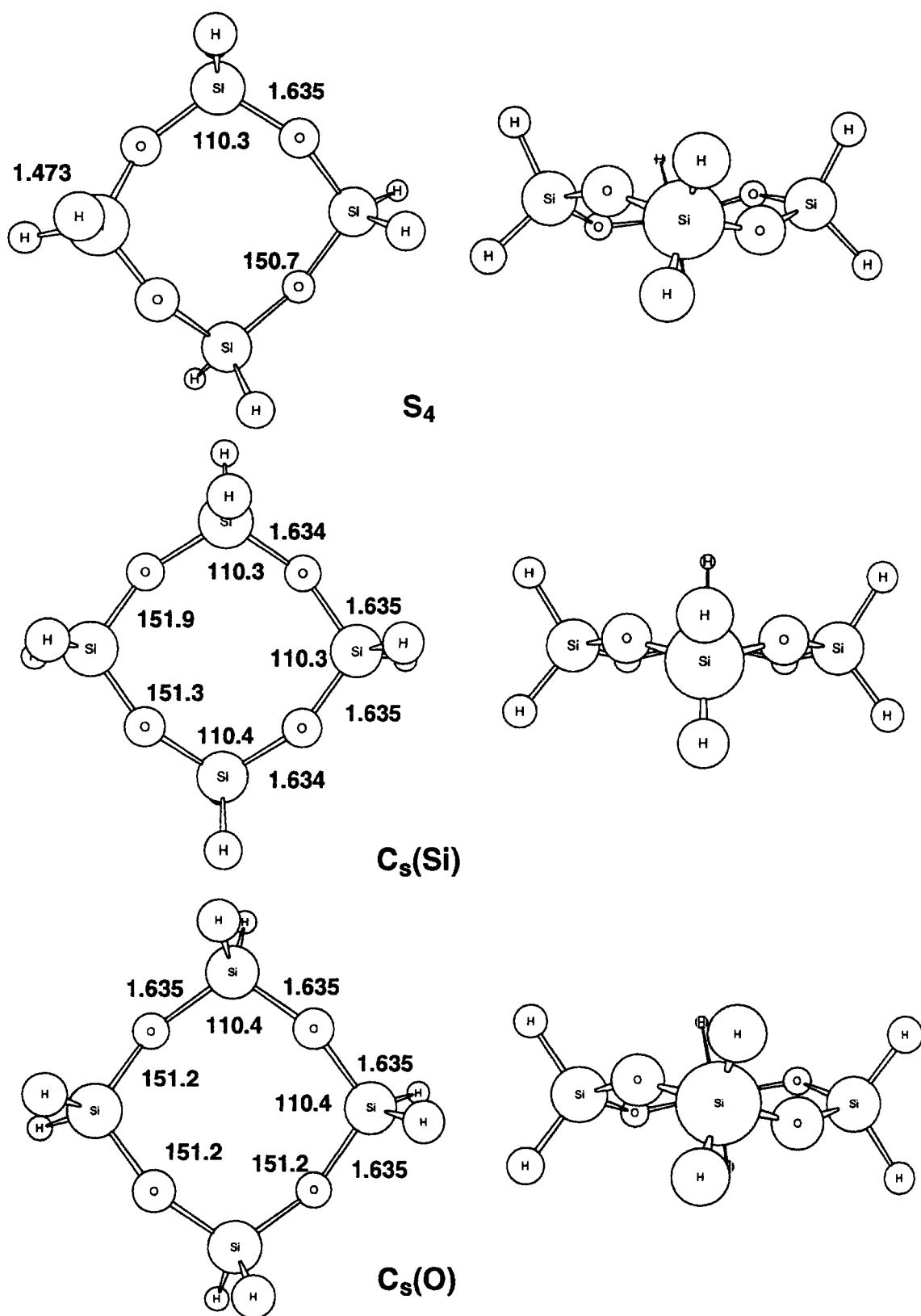


FIGURE 2. The HF/6-31G*-optimized geometries of D_4 [S_4 , $C_s(Si)$, and $C_s(O)$] in angstroms and degrees. Top views are on left side and side views are on right side.

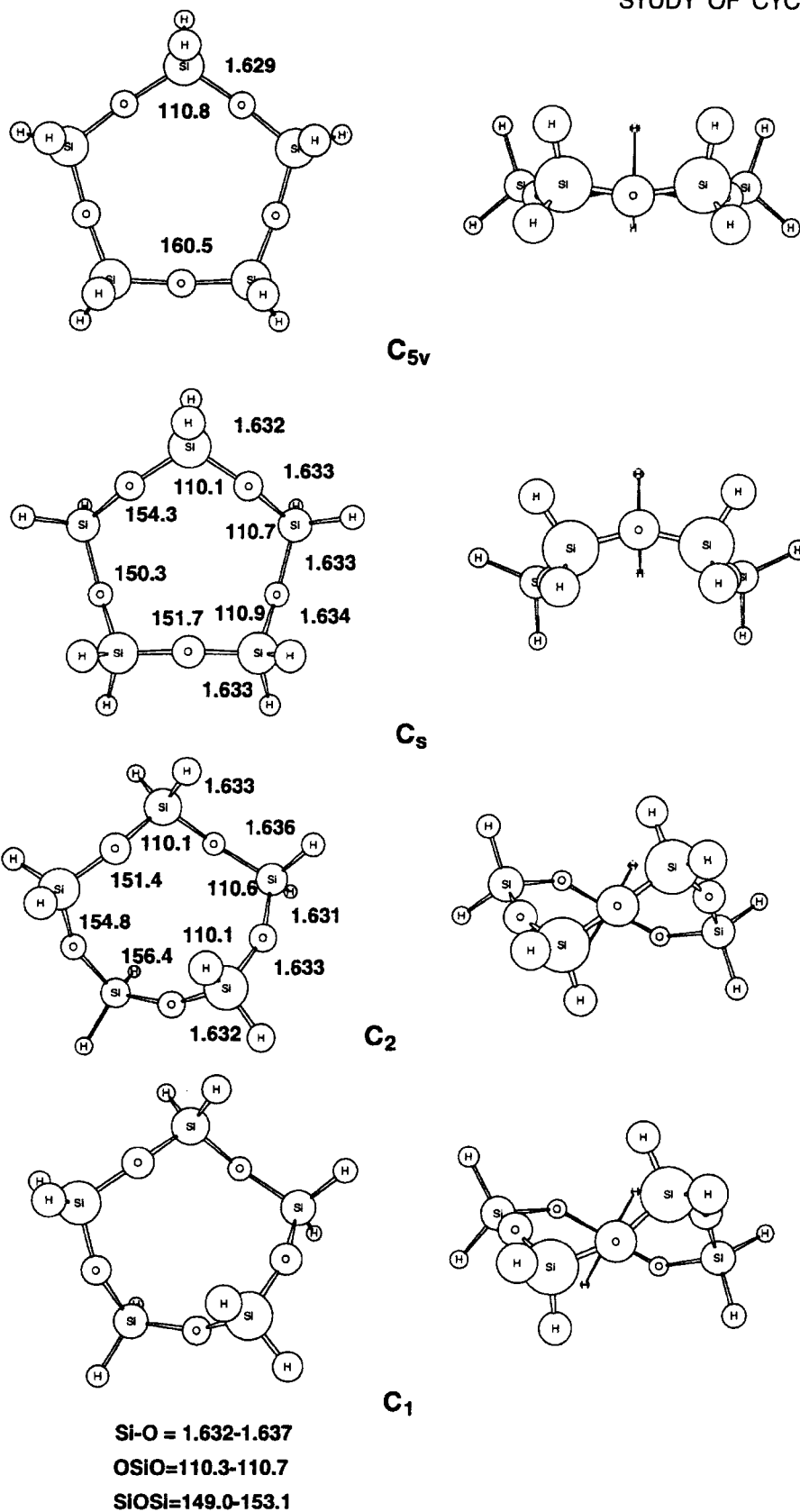


FIGURE 3. The HF/6-31G*-optimized geometries of D_5 (C_{5v} , C_s , C_2 , and C_1) in angstroms and degrees. Top views are on left side and side views are on right side.

TABLE I.
Total Energies (Hartree) and Number of Negative Eigenvalues for the D_n ($n = 3, 4$, and 5) Conformations.

| | | HF / 6-31G* | N.E. ^a | HF / 6-311G(d, p) | N.E. ^a | MP2 / 6-311G(d, p) ^b |
|-------|------------|-------------|-------------------|-----------------------|-------------------|-------------------------------------|
| D_3 | D_{3h} | -1095.11061 | 0 | -1095.24587 | 0 | — |
| D_4 | D_{4h} | -1460.15893 | 4 | -1460.34635 | 0 | — |
| | S_4 | -1460.15933 | 0 | -1460.34635 | — | — |
| | C_s (Si) | -1460.15927 | 1 | -1460.34635 | — | — |
| | C_s (O) | -1460.15932 | 1 | -1460.34635 | — | — |
| | C_1 | -1460.15927 | — | — | — | — |
| D_5 | D_{5h} | -1825.19900 | 9 | -1825.43571 | 0 | -1826.89036 |
| | C_{5v} | -1825.19925 | 4 | -1825.43571 | — | — |
| | C_s | -1825.20068 | 1 | -1825.43570 | 0 | -1826.89038 |
| | C_2 | -1825.20089 | 1 | -1825.43570 | 0 | -1826.89039 |
| | C_1 | -1825.20102 | 0 | -1825.43550 | 0 | -1826.89088 |

^aNegative Eigenvalues.^bMP2 single point energies at the HF / 6-311G(d, p) geometries.

respectively. As Table I shows, both structures are found to be minima on their potential energy surface as is the D_{3h} structure of D_3 at the same level of theory. These results for D_3 and D_4 are in good agreement with the previous experimental observations. At the HF/6-311G(d, p) level, however, the D_{4h} structure is the unique minimum of D_4 as already noted, while three conformers of D_5 (D_{5h} , C_{5v} , and C_2) have very similar energies despite the geometric differences. This is explained by the extremely flat vibrational surface of hydrogens for D_5 , based on the lower vibrational frequencies noted above for these structures. The D_{5h} structure is slightly more stable than C_1 at this level of calculation. Therefore, planar structures seem to be relatively stabilized at the HF/6-311G(d, p) level of theory in both D_4 and D_5 . However, the inclu-

sion of electron correlation via second order perturbation theory (MP2) reverses the order for D_5 , with the C_1 structure the most stable conformation of D_5 . Our final estimation for the energy difference between the D_{5h} and C_1 structures is 0.33 kcal/mol (0.28 kcal/mol after corrections for harmonic zero point vibrational effects) at the MP2/6-311G(d, p)/HF/6-311G(d, p) level. This is a very small difference.

Because of the very small energy differences among the D_5 isomers, we have investigated the effect of temperature ($T = 0$ to 500 K) on the relative stabilities of the four conformers of D_5 , by applying the Boltzmann equilibrium distribution to the MP2/6-311G(d, p) energies and HF/6-311G(d, p) structures and frequencies. The preceding discussions only depend on the electronic energy difference, related to the enthalpy term (H) of the free energy. The temperature effects also incorporate the entropy term (S):

$$P_T(j) = \frac{e^{-\Delta G_T(j)/RT}}{\sum_j e^{-\Delta G_T(j)/RT}}$$

In this expression, $\Delta G_T(j)$ is the Gibbs free energy of conformer j at temperature T , relative to the global minimum [$\Delta G_T(C_1) = 0$], and R is the ideal gas constant. The results of these calculations are summarized in Figure 5. As already noted, the distribution is 100% C_1 at 0 K. However, the importance of this structure decreases dramatically as temperature increases. At the same time, the importance of the C_{5v} and C_2 structures increase. Indeed, the C_{5v} structure makes the largest contribution of all temperatures except 0 K, and this contribution increases with increasing tempera-

TABLE II.
Relative Energies (kcal / mol) of the D_4 and D_5 Conformations.

| | | HF / 6-31G* | HF / 6-311G(d, p) | MP2 / 6-311G(d, p) ^a | +ZPC |
|-------|------------|----------------|--------------------------|--|-------|
| D_4 | D_{4h} | 0.00 | 0.00 | — | — |
| | S_4 | -0.25 | — | — | — |
| | C_s (Si) | -0.21 | — | — | — |
| | C_s (O) | -0.24 | — | — | — |
| | C_1 | -0.21 | — | — | — |
| D_5 | D_{5h} | 0.00 | 0.00 | 0.00 | 0.0 |
| | C_{5v} | -0.16 | 0.00 | — | — |
| | C_s | -1.05 | 0.006 | -0.01 | -0.01 |
| | C_2 | -1.19 | 0.006 | -0.02 | -0.02 |
| | C_1 | -1.27 | 0.13 | -0.33 | -0.28 |

^aMP2 single point energies at the HF / 6-311G(d, p) geometries.

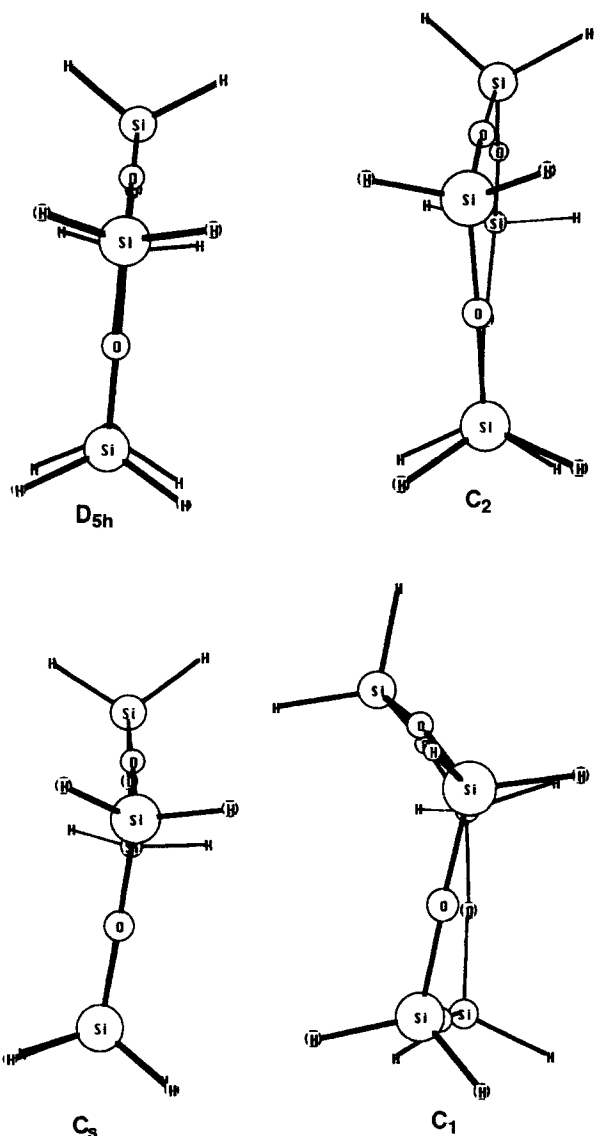


FIGURE 4. The end-on views of the HF / 6-311G(*d, p*)-optimized structures of D_5 (C_{5v} , C_5 , C_2 , and C_1). The arrows indicate the lowest vibrational mode.

ture. This means that the small electronic energy difference makes a rather minor contribution to the distribution at nonzero temperatures, and the entropy term is very important. The C_5 structure is found to have the largest entropy in this temperature range. The entropy decreases in the order $C_5 > C_2 > C_1 > D_{5h}$. As a result, the C_5 and C_2 conformers become very important.

In summary, the HF/6-311G(*d, p*) optimization is expected to give more reliable geometries compared with the HF/6-31G* level for D_n ($n = 3$ to 5) of cyclosiloxanes. At the highest levels of theory, the only minimum for $n = 4$ (D_4) occurs at the

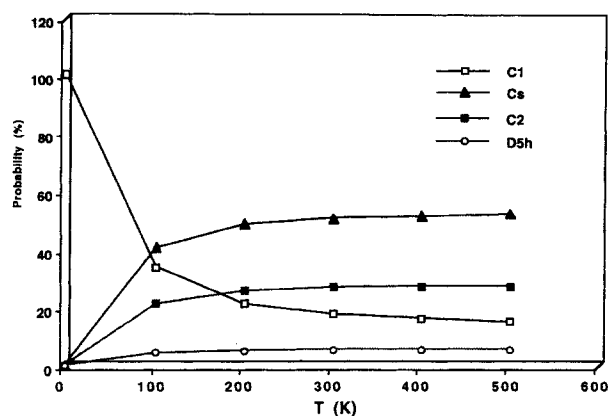


FIGURE 5. Equilibrium composition of D_5 in the temperature range from 0 to 500 K, as a plot of the percent probability versus T .

highly symmetric D_{4h} structure. In contrast, several nearly isoenergetic minima are found on the D_5 surface. These have C_1 , C_2 , C_5 , and D_{5h} symmetries. While the C_1 structure has the lowest MP2/6-311G(*d, p*)/HF/6-311G(*d, p*) energy, the D_5 molecule is expected to be highly fluxional, and the distribution of isomers is rather dependent on temperature, via entropic effects, as shown in Figure 5.

There have been several efforts to use *ab initio* calculations as an aid for developing molecular mechanics force fields (MMFF) for compounds that contain Si—O bonds (see, e.g., refs. 8b, 11, and 19). A particularly appealing alternative, general approach for such an endeavor has been suggested by Palmö et al.,²⁰ in which a full *ab initio* force constant matrix can be directly transformed onto a molecular mechanics force field. This method is independent of the details of the specific MMFF implementation. This method is especially appealing for highly fluxional compounds such as those of interest here, since the small off-diagonal force constants that are often neglected in such treatments are easily included with this method.

Acknowledgments

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